

MAGNESIUM-BASED CASTING ALLOYS HAVING IMPROVED ELEVATED TEMPERATURE PERFORMANCE

Patent Number: WO0144529

Publication date: 2001-06-21

Inventor(s): LABELLE PIERRE (CA); PEKGULERYUZ MIHRIBAN O (CA)

Applicant(s): NORANDA INC (CA); LABELLE PIERRE (CA); PEKGULERYUZ MIHRIBAN O (CA)

Requested Patent: WO0144529

Application Number: WO2000CA01527 20001214

Priority Number(s): US19990461538 19991215

IPC Classification: C22C23/02

EC Classification:

Equivalents:

Abstract

A magnesium-based casting alloy having good salt-spray corrosion resistance and improved creep resistance, tensile yield strength and bolt-load retention, particularly at elevated temperatures of at least 150 DEG C, is provided. The inventive alloy comprises, in weight percent, 2 to 9% aluminum and 0.5 to 7% strontium, with the balance being magnesium except for impurities commonly found in magnesium alloys.

Data supplied from the esp@cenet database - I2

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44529 A1

(51) International Patent Classification⁷: C22C 23/02

(74) Agents: DUBUC, Jean, H. et al.; Goudreau Gage Dubuc,
The Stock Exchange Tower, 800 Place Victoria, Suite 3400,
P.O. Box 242, Montreal, Quebec H4Z 1E9 (CA).

(21) International Application Number: PCT/CA00/01527

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(22) International Filing Date:
14 December 2000 (14.12.2000)

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language: English

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

(26) Publication Language: English

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(30) Priority Data:
09/461,538 15 December 1999 (15.12.1999) US

(71) Applicant (*for all designated States except US*): NO-RANDA INC. [CA/CA]; BCE Place, 181 Bay Street, Suite 4100, P.O. Box 755, Toronto, Ontario M5J 2T3 (CA).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): PEKGULERYUZ, Mihriban, O. [CA/CA]; 213-165 Frobisher, Pointe-Claire, Quebec H9R 4R8 (CA). LABELLE, Pierre [CA/CA]; 137 Chemin du Lac Maillé, St-Hippolyte, Quebec J8A 1J8 (CA).

A1

WO 01/44529

(54) Title: MAGNESIUM-BASED CASTING ALLOYS HAVING IMPROVED ELEVATED TEMPERATURE PERFORMANCE

(57) Abstract: A magnesium-based casting alloy having good salt-spray corrosion resistance and improved creep resistance, tensile yield strength and bolt-load retention, particularly at elevated temperatures of at least 150 °C, is provided. The inventive alloy comprises, in weight percent, 2 to 9% aluminum and 0.5 to 7% strontium, with the balance being magnesium except for impurities commonly found in magnesium alloys.

MAGNESIUM-BASED CASTING ALLOYS HAVING IMPROVED
ELEVATED TEMPERATURE PERFORMANCE

FIELD OF THE INVENTION

5 The present invention generally relates to magnesium based casting alloys having improved elevated temperature performance and more particularly relates to magnesium-aluminum-strontium alloys having good salt-spray corrosion resistance and good creep resistance, tensile yield strength and bolt-load retention, particularly at elevated temperatures of at least 150°C.

BACKGROUND OF THE INVENTION

10 Magnesium-based alloys have been widely used as cast parts in the aerospace and automotive industries and are mainly based on the following four systems:

- 15 Mg-Al system (*i.e.*, AM20, AM50, AM60);
- Mg-Al-Zn system (*i.e.*, AZ91D);
- Mg-Al-Si system (*i.e.*, AS21, AS41); and
- Mg-Al-Rare Earth system (*i.e.*, AE41, AE42).

20 Magnesium-based alloy cast parts can be produced by conventional casting methods which include diecasting, sand casting, permanent and semi-permanent mold casting, plaster-mold casting and investment casting.

25 These materials demonstrate a number of particularly advantageous properties that have prompted an increased demand for magnesium-based alloy cast parts in the automotive industry. These properties include low density, high strength-to-weight ratio, good castability, easy machineability and good damping characteristics.

AM and AZ alloys, however, are limited to low-temperature applications where they are known to lose their creep resistance at temperatures above 140°C. AS and AE alloys, while developed for higher temperature applications, offer only a small improvement in creep resistance and/or are expensive.

It is therefore an object of the present invention to provide relatively low cost magnesium-based alloys with improved elevated-temperature performance.

It is a more particular object to provide relatively low cost magnesium-aluminum-strontium alloys with good creep resistance, tensile yield strength and bolt-load retention, particularly at elevated temperatures of at least 150°C, and good salt-spray corrosion resistance.

SUMMARY OF THE INVENTION

The present invention therefore provides a magnesium-based casting alloy comprising, in weight percent, 2 to 9% aluminum and 0.5 to 7% strontium with the balance being magnesium except for impurities commonly found in magnesium alloys.

The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Particular features of the disclosed invention are illustrated by reference to the accompanying drawings in which:

FIG. 1 is a photomicrograph showing the microstructure of a diecast alloy of the present invention, hereinafter referred to as alloy A1;

FIG. 2 is a photomicrograph showing the microstructure of another diecast alloy of the present invention, hereinafter referred to as alloy A2;

5 FIG. 3 is a photomicrograph showing the microstructure of permanent mold cast alloy AD9; and

FIG. 4 is a photomicrograph showing the microstructure of permanent mold cast alloy AD10.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

10 The magnesium-based casting alloys of the present invention are relatively low cost alloys that demonstrate improved creep resistance, tensile yield strength and bolt-load retention at 150°C. The inventive alloys also demonstrate good salt-spray corrosion resistance.

15 As a result of the above-identified properties, the inventive alloys are suitable for use in a wide variety of applications including various elevated temperature automotive applications such as automotive engine components and housings for automotive automatic transmissions.

20 The inventive alloys generally will have a preferred average % creep deformation at 150°C of $\leq 0.06\%$ for diecast alloys and $\leq 0.03\%$ for permanent-mold cast alloys. In addition, the alloys generally will have an average bolt-load-loss (measured as additional angle to re-torque) at 150°C of $\leq 6.3^\circ$ for alloys in the diecast state and $\leq 3.75^\circ$ for alloys in the permanent-mold cast state.

25 In regard to tensile properties, the inventive alloys will generally have an average tensile yield strength (ASTM E8-99 and E21-92 at 150°C) of > 100 megapascals (MPa) for diecast alloys and > 57 MPa for permanent-mold cast alloys.

The average resistance of the inventive alloys to salt-spray corrosion, when measured in accordance with ASTM B117, is preferably ≤ 0.155 milligrams per square centimeter per day ($\text{mg}/\text{cm}^2/\text{day}$) for alloys in the diecast state.

5 In general, the magnesium-based alloys of the present invention are 100% crystalline alloys that contain, in weight percent, 2 to 9% aluminum and 0.5 to 7% strontium, with the balance being magnesium. Main impurities commonly found in magnesium alloys, namely - iron (Fe), copper (Cu) and nickel (Ni), are preferably kept below the following 10 amounts(by weight): Fe $\leq 0.004\%$; Cu $\leq 0.03\%$; and Ni $\leq 0.001\%$ to ensure good salt-spray corrosion resistance.

In addition to the above components, the alloys of the present invention may contain the elements manganese (Mn) and/or zinc (Zn) in the following proportions (by weight): 0 - 0.60% Mn; and 0 - 0.35% Zn.

15 In a preferred embodiment, the inventive magnesium-based alloys contain, in weight percent, 4 to 6% aluminum, 1 to 5% strontium (more preferably 1 to 3%), 0.25 to 0.35% manganese and 0 to 0.1% zinc, with the balance magnesium. In yet a more preferred embodiment, the inventive alloys contain, in weight percent, 4.5 to 5.5% aluminum, 1.2 to 20 2.2% strontium, 0.28 to 0.35% manganese and 0 to 0.05% zinc, with the balance magnesium.

25 The inventive alloys may advantageously contain other additives provided any such additives do not adversely impact upon the elevated temperature performance and salt-spray corrosion resistance of the inventive alloys.

The inventive alloy can be produced by conventional casting methods which include diecasting, permanent and semi-permanent mold

casting, sand-casting, squeeze casting and semi-solid casting and forming.

It is noted that such methods involve solidification rates of < 10²K/sec.

In a preferred embodiment, the alloy of the present invention is prepared by melting a magnesium alloy (e.g., AM50), stabilizing the 5 temperature of the melt between 675 and 700°C, adding a strontium aluminum master alloy (e.g., 90-10 Sr-Al master alloy) to the melt and then casting the melt into a die cavity using either diecasting or permanent mold casting techniques.

The microstructure of the alloys obtained is described as 10 follows. The matrix is made up of grains of magnesium having a mean particle size of from about 10 to about 200 micrometers (μm) (preferably from about 10 to about 30 μm for alloys in the diecast state and greater than 30 μm for alloys in the permanent mold cast state). The matrix is reinforced by precipitates of intermetallic compounds dispersed homogeneously 15 therein, preferably at the grain boundaries, that have a mean particle size of from about 2 to about 100 μm (preferably from about 5 to about 60 μm for diecast alloys and slightly larger for permanent mold cast alloys).

Scanning electron microscopy of the inventive alloys show 20 that the diecast alloys contain Al-Sr-Mg containing second phases approximately 2 to 30 μm long and approximately 1 to 3 μm thick while the permanent mold cast alloys contain Al-Sr-Mg containing second phases approximately 10 to 30 μm long and approximately 2 to 10 μm thick.

As best shown by the scanning electron micrographs of FIGS. 1 and 2, the microstructures of inventive diecast alloys A1 and A2, which 25 have a chemical composition as described in Table 1 hereinbelow, contain Al-Sr-Mg containing second phases approximately 25 μm long and 2 μm thick.

As best shown by the scanning electron micrographs of FIGS. 3 and 4, the microstructures of inventive permanent mold cast alloys AD9 and AD10, which have a chemical composition as described in Table 1 hereinbelow, contain Al-Sr-Mg containing second phases approximately 5 $30\mu\text{m}$ long and $5\mu\text{m}$ thick.

The present invention is described in more detail with reference to the following Examples which are for purposes of illustration only and are not to be understood as indicating or implying any limitation on the broad invention described herein.

10

WORKING EXAMPLES

Components Used

AM50 - a magnesium alloy containing 4.17% by weight of aluminum and 0.32% by weight of manganese obtained from Norsk-Hydro, Bécancour, Québec, Canada.

90-10 Sr-Al - a strontium-aluminum master alloy containing 90% by weight strontium and 10% by weight aluminum obtained from Timminco Metals, a division of Timminco Ltd., Haley, Ontario, Canada.

AZ91D - a magnesium alloy containing 8.9 (8.3-9.7)% by weight aluminum, 0.7 (0.35-1.0)% by weight zinc and 0.18 (0.15-0.5)% by weight manganese obtained from Norsk-Hydro.

AM50 - a magnesium alloy containing 4.7 (4.4-5.5)% by weight aluminum and 0.34 (0.26-0.60)% by weight manganese obtained from Norsk-Hydro.

AS41 - a magnesium alloy containing 4.2-4.8 (3.5-5.0)% by weight aluminum and 0.21 (0.1-0.7)% by weight manganese obtained from
The Dow Chemical Company, Midland, MI.

5 AM60B - a magnesium alloy containing 5.7 (5.5-6.5)% by weight aluminum and 0.24 (0.24-0.60)% by weight manganese obtained from Norsk-Hydro.

10 AE42 - a magnesium alloy containing 3.95 (3.4-4.6)% by weight aluminum and 2.2 (2.0-3.0)% by weight of rare earth elements and a minimum of 0.1% by weight manganese obtained from Magnesium Elektron, Inc., Flemington, NJ.

A380 - an aluminum alloy containing 7.9% by weight silicon and 2.1% by weight zinc obtained from Roth Bros. Smelting Corp., East Syracuse, NY.

Sample Preparation

Alloys A1 and A2

20 Two different alloys were prepared by: charging ingots of AM50 into an 800 kilogram (kg) crucible positioned in a Dynarad MS-600 electric resistance furnace; melting the charge; stabilizing the temperature of the melt at 670°C; and adding 90-10 Sr-Al master alloy to the melt.

25 The temperature of the melt was maintained at 670°C for 30 minutes, stirred and then chemical analysis samples taken by pouring equal quantities of the melt into copper spectrometer molds.

The chemical analysis samples were analyzed using ICP mass spectrometry. The chemical composition of the prepared alloys, namely -

A1 and A2, are shown in Table 1 hereinbelow. The recovery rate of strontium was determined to be approximately 90%.

The temperature of the melt was cooled to 500°C while the ICP chemical analysis was carried out on the melt samples. The melt temperature was monitored by both a furnace controller and by a hand-held K-type thermocouple connected to a Fluke-51 digital thermometer.

During melting and holding, the melt was protected under a gas mixture of 0.5% SF₆- 25% CO₂, balance air.

The molten metal was die-cast using a ~~600-tonne Prince~~
 10 (Prince-629) cold-chamber diecasting machine to produce diecast flat-tensile specimens measuring 8.3 x 2.5 x 0.3cm (gage 1.5 x 0.6cm), round tensile specimens measuring 10 x 1.3cm (gage 2.54 x 0.6cm), cylindrical test specimens measuring 4 x 2.5cm and corrosion test plates measuring 10 x 15 x 0.5cm.

15 Operating parameters used for the cold-chamber diecasting machine are shown below.

Operating Parameters	AZ91D	AS41	AE42	AM60	A380	A1	A2
Alloy Temp. (°C)	680	720	750	750	750	720	720
Temperature Of Metal Before Injection (°C)	250	300	300	300	300	275	275
Pressure (MPa)	13.8	13.8	13.8	13.8	13.8	13.8	13.8
Piston length (cm)	3.8/29.2	3.8/29.2	3.8/29.2	3.8/29.2	3.8/29.2	3.8/29.2	3.8/29.2
Base speed (cm/sec)	28-51	28-51	28-51	28-48	28-48	28-51	28-51
Fast speed (cm/sec)	384-516	315-498	368-587	417	312-330	384-516	384-516
Average cycle time (sec)	44-58	43-73	46-50	43	42-49	44-58	44-58

Operating Parameters	AZ91D	AS41	AE42	AM60	A380	A1	A2
Average die opening time (sec)	30-44	29-54	32-36	18-29	18-35	30-44	30-44
Die Lubricant	Rdl-3188						

Alloys AD9-AD14

Six different alloys were prepared by: charging 250g ingots of 5 AM50 into a 2 kg steel crucible positioned in a Lindberg Blue-M electric resistance furnace; melting the charge; stabilizing the temperature of the melt between 675 and 700°C; and adding small pieces of 90-10 Sr-Al master alloy to the melt.

The temperature of the melt was maintained at either 675°C 10 for 30 minutes or at 700°C for 10 minutes, stirred and then chemical analysis samples taken by pouring equal quantities of the melt into copper spectrometer molds.

The chemical analysis samples were analyzed using ICP mass spectrometry. The chemical composition of the prepared alloys, namely - 15 AD9 to AD14, are shown in Table 1 hereinbelow. The recovery rate of strontium was determined to be 87-92%.

The temperature of the melt was measured by a K-type Chromel-Alumel thermocouple immersed in the melt.

During melting and holding, the melt was protected under a 20 gas mixture of 0.5% SF₆, balance CO₂.

The molten metal was permanent mold cast using copper permanent molds having mold cavities measuring 3cm in height with each mold cavity having a top diameter of 5.5cm and a bottom diameter of 5cm.

Alloys AC2, AC4, AC6, AC9 and AC10

Five different alloys were prepared in accordance with the test procedure detailed above for Alloys AD9 - AD14.

Chemical analysis samples were taken from the melt and analyzed using ICP mass spectrometry. The chemical composition of the prepared alloys, namely - AC2, AC4, AC6, AC9 and AC10, are shown in Table 1 hereinbelow. The recovery rate of strontium was determined to be 87.92%.

The molten metal was permanent mold cast using an H-13 (mild) steel permanent mold. The mold contained cavities for two ASTM standard test bars each measuring 14.2cm in length and 0.7cm in depth or thickness. Grip width was 1.9cm while gage length and gage width was 5.08cm and 1.27cm, respectively. The mold was provided with a sprue, riser and gating system to bottom-feed the two tensile bar cavities.

15

TABLE 1

ALLOY	CHEMICAL COMPOSITION								
	Al, wt%	Sr, wt%	Mn, wt%	Zn (ppm)	Fe (ppm)	Cu(ppm)	Ni (ppm)	Si (ppm)	Ca (ppm)
AM50	5.0	-	0.32	200	20	10	10	70	20
90-10 Sr-Al master alloy	10	90							
A1	4.90	1.74	0.26	94	23	4	3	34	18
A2	4.85	1.23	0.29	94	11	2	3	47	17
AD9	4.96	0.94	0.28	56	<10	<2	<2	-	17
AD10	5.07	1.21	0.29	61	<10	<2	<2	-	18
AD11	5.00	1.54	0.28	54	<10	<2	<2	-	18
AD12	5.18	2.31	0.28	54	<10	<2	<2	-	18

ALLOY	CHEMICAL COMPOSITION								
AD13	5.10	3.77	0.28	54	<10	<2	<2	-	18
AD14	5.71	6.89	0.28	54	<10	<2	<2	-	18
AC2	4.90	1.59	0.30	43	60	<2	<2	-	<10
AC4	4.70	1.26	0.33	78	84	122	7	-	35
AC6	4.89	1.22	0.32	69	41	127	9	-	40
AC9	4.82	1.07	0.32	42	39	82	3	-	31
AC10	5.08	1.46	0.29	52	39	150	2	-	8

Various properties of the alloys were then tested as set forth below and compared against other magnesium alloys and aluminum alloy

5 A380.

Test Methods

The diecast and permanent mold cast test specimens were subjected to the following tests:

10

Creep Resistance or Creep Extension

The creep resistance of the diecast and permanent mold cast test specimens was measured in accordance with ASTM E139-83. In particular, test specimens were exposed to air for a period of 60 minutes and 15 then subjected, for a period of 200hr, to a constant stress of 35 MPa via an Applied Test Systems, Inc. (ATS) Lever Arm Tester-2320 creep testing machine while being maintained at a temperature of 150°C. The gage length of each test specimen was then measured and the difference between the original gage length (i.e., 1.27cm) and the gage length of each specimen at 20 the end of the 200hr test period was determined. The difference in gage

length determined for each test specimen was then divided by 1.27cm and the result reported as a percent (%).

Bolt-Load-Retention or Bolt-Load-Loss

5 The bolt-load-retention of the diecast test specimens was measured in accordance with the following procedure: diecast cylinders of the alloys were used to machine disc samples measuring 25.4x9mm. A hole having a diameter of 8.4mm was then drilled in the middle of each sample. An M8 steel bolt and nut (1.25 pitch) were then screwed with a torque-wrench into each disc sample using a washer of 15.75mm OD and 8.55 ID 10 and torqued to 265 lbs.in (30Nm). A special set-up was used to measure the initial angle to which the bolt had to be rotated to reach the prescribed torque.

15 The special set-up consisted of a 360° mild steel protractor fabricated by the machine shop at Noranda Inc. Technology Center. The protractor had a central hole in the shape of an M10 nut, machined to receive and fix the test specimen in place. A machined M8 socket was used to adapt the hole to an M8 bolt. The protractor was bolted to a table to counteract the rotation force applied during torquing with a digital torque wrench (model 20 Computorq II -64-566 manufactured by Armstrong Tool, USA).

25 The bolted samples were then immersed in an oil bath having a temperature of 150°C and were kept in the oil bath for 48 hours where the bolts lost some torque due to stress relaxation. The samples were then removed from the oil bath, cooled to room temperature and the bolts retightened to the initial torque of 265 lbs.in (30Nm). The additional angle required to reach the initial torque was then measured and this value used as a measure of bolt-loosening. The results are reported in degrees (°).

The bolt-load-retention of the permanent mold cast test specimens was measured in accordance with the following procedure:

permanent mold cast disc samples of the alloys were machined to discs measuring 35x11mm. A hole having a diameter of 10.25 was then drilled in the middle of each sample. An M10 steel bolt and nut (1.5 pitch) were then screwed with a torque-wrench into each disc sample using a washer of 5 19.75mm OD and 10.75 ID and torqued to 440 lbs.in (50Nm). A special set-up was used to measure the initial angle to which the bolt had to be rotated to reach the prescribed torque. The set-up was identical to that noted above, except that a machined M8 bolt was not used to adapt the central hole to the M8 bolt. The bolted samples were then immersed in an oil bath having a 10 temperature of 150°C and were kept in the oil bath for 48 hours where the bolts lost some torque due to stress relaxation. The samples were then removed from the oil bath, cooled to room temperature and the bolts re-tightened to the initial torque of 440 lbs.in (50Nm). The additional angle required to reach the initial torque was then measured and this value used as 15 a measure of bolt-loosening. The results are reported in degrees (°).

Tensile Properties

Tensile properties (i.e., tensile yield strength, ultimate tensile strength and elongation) at an elevated temperature of 150°C and at room 20 temperature were measured in accordance with ASTM E8-99 and E21-92. An Instron servovalve hydraulic Universal Testing Machine (model number 8502-1988) equipped with an Instron oven (model number 3116) and an Instron extensiometer (model number 2630-052) were used in conjunction with the subject test methods.

25 For tensile testing at 150°C, test specimens were clamped within the test assembly and heated to a temperature of 150°C and then maintained at this temperature for a period of 30 minutes. Specimens were then tested at 0.13cm/cm/min through yield and at 1.9cm/min to failure.

For room temperature tensile testing, specimens were tested at 0.7MPa/min through yield and at 1.9cm/min to failure.

Tensile yield strength was determined by passing a tangent to the part of the stress-strain curve between 20.5-34.5 MPa and by passing a 5 second line parallel to the one intersecting the y-axis at a 0.2% extension. Results are reported in megapascals (MPa).

Ultimate tensile strength was determined as the stress at rupture or as the maximum stress in the stress-strain curve. Results are reported in MPa.

10 Elongation was determined by measuring the gage length of each test specimen before and after testing. Results are reported in percent (%).

Salt-Spray Corrosion Resistance

15 The resistance of the diecast corrosion test plate test specimens to corrosion was measured in accordance with ASTM B117. In particular, specimens were cleaned using a 4% NaOH solution at 80°C, rinsed in cold water and dried with acetone. The specimens were then weighed and then vertically mounted at 20° from the vertical axis within a SINGLETON salt-spray test cabinet (model number SCCH #22). The vertically mounted specimens were then exposed to a 5% NaOH/distilled water fog for a period of 200hr. During the test period, the fog tower was adjusted to a collection rate of 1cc/hr and the parameters of the cabinet checked every 2 days. At the end of the 200hr test period, the specimens were removed, washed in cold water and cleaned in a chromic acid solution (i.e., chromic acid containing silver nitrate and barium nitrate) as per ASTM B117. The samples were then re-weighed and the weight change per sample determined. The results are reported in milligrams per square centimeter per day (mg/cm²/day).

EXAMPLES 1 AND 2 AND COMPARATIVE EXAMPLES C1 TO C5

In these examples diecast specimens prepared in accordance with the teachings of the present invention and diecast magnesium alloys AZ91D, AE42, AS41 and AM60B and aluminum alloy A380 were tested for creep resistance, bolt-load retention, various tensile properties at both room temperature and at 150°C and salt-spray corrosion resistance. The results are tabulated in Table 2.

10

TABLE 2
Summary of Examples 1 and 2 and Comparative Examples C1 to C5

EXAMPLE	1	2	C1	C2	C3	C4	C5
ALLOY	A1	A2	AZ91D	AE42	AS41	AM60B	A380
Properties:							
Creep Extension (%) at 150°C							
Run 1	0.05%	0.12%	1.64%	0.09%	0.168 %	-	0.192%
Run 2	0.03%	0.07%	0.90%	0.06%	0.102 %	-	0.154%
Run 3	0.02%	0.02%	1.08%	0.05%	0.12%	-	0.18%
AVERAGE	0.03%	0.06%	1.21%	0.07%	0.13%	-	0.18%
Bolt-Load-Loss (°) at 150°C							
Run 1	6.0°	6.0°	14.0°	9.0°	10.5°	-	2.0°
Run 2	6.0°	6.5°	14.5°	7.5°	11.0°	-	2.0°
AVERAGE	6.0°	6.3°	14.3°	8.3°	10.8°	-	2.0°

EXAMPLE	1	2	C1	C2	C3	C4	C5
Tensile Properties at 150° C	A291	A492	J541	AM60	A780		
Yield Strength (MPa)							
Run 1	119.9	100.8	108.2	85.4	87.7		168.5
Run 2	111.1	105.0	99.5	96.2	96.3		147.6
Run 3	112.8	100.0	104.4	87.2	92.0		152.0
Run 4	108.5	106.0	-	85.0	98.4		146.5
Run 5	106.9	100.0	106.9	89.7	89.6		158.6
Run 6	100.0	96.6	106.9	82.8	89.6		148.2
Run 7	103.4	96.6	103.4	86.2	93.1		137.9
AVERAGE	108.9	100.7	104.9	87.5	92.4		151.3
Ultimate Tensile Strength (MPa)							
Run 1	188.3	150.8	179.9	139.0	154.0		293.0
Run 2	168.1	143.3	161.6	162.6	153.0		235.7
Run 3	171.1	149.7	174.3	152.3	155.3		264.3
Run 4	161.1	157.9	-	143.5	147.9		259.9
Run 5	158.6	148.3	169.0	137.9	144.8		251.7
Run 6	158.6	144.8	169.0	127.6	137.9		255.1
Run 7	151.7	148.3	165.5	137.9	155.1		220.6
AVERAGE	165.4	149.0	169.9	143.0	149.7		254.3
Elongation %							
Run 1	11.7	19.3	20.6	16.1	19.8		4.4

EXAMPLE	1	2	C1	C2	C3	C4	C5
Ru 2	8.0	9.2	12.5	24.4	20.4		3.1
Ru 3	22.0	17.6	12.6	30.2	19.5		7.5
Rn 4	8.2	24.9	-	25.6	7.4		7.5
Run5	22.1	11.7	19.5	21.6	17.6		4.5
Rn 6	14.3	23.4	11.7	22.3	16.7		7.9
Run7	7.8	19.5	19.5	24.6	17.8		4.5
AERAGE	13.4%	17.9%	16%	23.5%	17%		6.7%
Tnsile Properties at Room Temperature							
Yiel Strength (MPa)							
1	136.7	136.6	154.1	132.0	118.1		141.9
Ru 2	146.0	136.2	156.9	131.5	139.3		157.8
Run	139.7	136.2	150.8	130.9	136.8		160.6
Rn 4	146.6	136.0	154.8	131.2	135.7		156.4
Run 5	136.2	135.3	-	131.0	129.6		155.9
Run 6	151.7	141.4	162.1	137.9	148.2		162.0
Run 7	144.8	137.9	158.6	137.9	151.7		148.2
Run 8	148.3	141.4	158.6	137.9	131.0		158.6
AVERAGE	143.7	137.6	156.6	133.8	123.8		155.2
Ultimate Tensile Strength (MPa)							
Run 1	206.8	228.0	257.0	240.3	255.4		247.4
Run 2	215.5	223.1	249.4	221.6	231.0		233.0

EXAMPLE	1	2	C1 A1	C2 A2	C3 A3	C4 A4(0)	C5
Run 3	215.3	236.5	220.7	212.8	241.5		332.5
Run 4	222.9	228.5	231.5	240.3	254.6		312.1
Run 5	241.6	238.2	-	240.7	262.6		323.5
Run 6	186.2	231.0	231.0	206.9	196.5		310.3
Run 7	-	234.5	227.6	227.6	217.2		251.7
Run 8	193.1	241.4	248.3	224.1	231.0		317.2
AVERAGE	211.6	232.7	237.9	226.8	236.3		291.0
Elongation %							
Run 1	3.7	7.6	5.6	13.2	11.0		1.8
Run 2	4.1	6.4	4.4	8.3	5.4		1.7
Run 3	5.0	9.2	3.6	5.6	8.0		4.7
Run 4	5.0	8.2	3.5	12.4	9.8		4.0
Run 5	7.9	8.4	4.3	10.2	10.1		3.0
Run 6	3.7	6.2	5.0	6.2	3.3		4.4
Run 7	2.5	11.2	5.0	10.0	4.4		2.2
Run 8	2.5	11.2	6.2	8.7	7.8		3.4
AVERAGE	4.3%	8.6%	4.7%	9.3%	7.4%		3.2%
Salt-Spray Corrosion Rate (mg/cm ² /day)							
Run 1	0.104	0.119	0.127	0.172	0.019	0.307	0.322
Run 2	0.097	0.105	0.097	0.251	0.174	0.236	0.330
Run 3	0.057	0.197	0.085	0.144	0.317	0.175	0.380

	¹⁹ A2	AE	AS	AM50	A380		
EXAMPLE	1	2	C1	C2	C3	C4	C5
AVERAGE	0.086	0.155	0.103	0.189	0.170	0.260	0.344

5 A review of the average creep extension, bolt-load-loss, tensile properties and salt-spray corrosion rate values in Table 2 indicates that the overall elevated temperature performance as compared to magnesium alloys AZ91D, AE42, AS41 and AM60B and aluminum alloy A380.

In particular, Examples 1 and 2 demonstrated improved creep resistance over comparative Examples C1(AZ91D), C2(AE42) and C5(A380) and better bolt-load retention (smaller angle of loss) than Comparative
10 Examples C1 to C3(AZ91D, AE42 and AS41).

In terms of tensile properties, Examples 1 and 2 demonstrated improved yield strength (at room temperature and at 150°C) over Comparative Examples C2(AE42) and C3(AS41) and improved elongation (at room temperature and at 150°C) over Comparative Example C5(A380).

15 Examples 1 and 2 further demonstrated improved salt-spray corrosion resistance over Comparative Examples C2(AE42), C3(AS41), C4(AM60B) and C5(A380) and comparable salt-spray corrosion resistance to that demonstrated by Comparative Example C1(AZ91D).

20 EXAMPLES 3 TO 8 AND COMPARATIVE EXAMPLES C6 TO C10

In these examples permanent mold cast disc specimens prepared in accordance with the present invention and permanent mold cast magnesium alloys AZ91D, AM50, AS41 and AE42 and aluminum alloy A380 were tested for bolt-load retention. The results are tabulated in Table 3.

TABLE 3

Summary of Examples 3 to 8 and Comparative Examples C6 to C10

EXAMPLE	3	4	5	6	7	8	C6	C7	C8	C9	C10
ALLOY	AD90	AD10	AD11	AD12	AD13	AD14	AZ91D	AM50	AS41	AE42	A380
Properties											
Bolt-Load-Loss (°)											
Run 1	3.25°	2.5°	2.5°	4.5°	2.0°	2.0°	9.5°	4.75°	3.0°	3.0°	2.0°
Run 2	2.75°	3.0°	3.0°	3.0°	2.5°	2.0°	9.5°	7.5°	6.0°	3.0°	2.0°
Run 3	-	-	-	-	-	-	8.5°	7.0°	-	4.5°	-
Run 4	-	-	-	-	-	-	9.5°	7.5°	-	3.5°	-
Run 5	-	-	-	-	-	-	8.5°	-	-	7.0°	-
AVERAGE	3.0°	2.75°	2.75°	3.75°	2.25°	2.0°	9.1°	6.7°	4.5°	4.2°	2.0°

By way of the average bolt-load-loss values shown in Table 3,

5 it can be seen that the permanent mold cast alloys of the present invention (i.e., Examples 3 to 8) demonstrate improved bolt-load retention (smaller angle of loss) when compared to magnesium alloys AZ91D, AM50, AS41 and AE42 (i.e., C6 to C9) and comparable bolt-load retention to that demonstrated by aluminum alloy A380 (i.e., C10).

10

EXAMPLES 9 TO 12 AND COMPARATIVE EXAMPLES C11 TO C13

In these examples permanent mold cast ASTM standard flat tensile specimens prepared in accordance with the present invention and permanent mold cast magnesium alloys AZ91D and AE42 and aluminum alloy A380 were tested for creep resistance. The results are tabulated in Table 4.

TABLE 4
Summary of Examples 9 to 12 and Comparative Examples C11 to C13

EXAMPLE	9	10	11	12	C11	C12	C13
ALLOY	AC9	AC4	AC6	AC10	AZ91D	AE42	A380
Properties:							
Creep Extension (%) at 150°C							
Run 1	0.012%	0.006%	0.0215%	0.03%	0.136%	0.035%	0.092%
Run 2	-	-	0.029%	-	-	0.014%	0.099%
AVERAGE	0.01%	0.01%	0.03%	0.03%	0.136%	0.03%	0.096%

5 By way of the average creep extension values shown in Table 4, it can be seen that the permanent mold cast alloys of the present invention (i.e., Examples 9 to 12) demonstrate improved creep resistance at 150°C when compared to magnesium alloys AZ91D and A380 (i.e., C11 and C13) and comparable creep resistance to that demonstrated by magnesium alloy 10 AE42 (i.e., C12).

EXAMPLES 13 TO 16 AND COMPARATIVE EXAMPLES C14 TO C16

In these examples permanent mold cast ASTM standard flat tensile specimens prepared in accordance with the present invention and 15 permanent mold cast magnesium alloys AZ91D and AE42 and aluminum alloy A380 were tested for tensile properties at 150°C. The results are tabulated in Table 5.

TABLE 5

Summary of Examples 13 to 16 and Comparative Examples C14 to C16

EXAMPLE	13	14	15	16	C14	C15	C16
ALLOY	AC9	AC6-AC4	AC10	AC2	AZ91D	AE42	A380
Properties:							
Tensile Properties at 150°C							
Yield Strength (MPa)							
Run 1	56.5	59.3	62.0	69.7	81.2	43.9	124.3
Run 2	58.6	66.7	62.1	62.9	78.7	48.0	126.4
Run 3	-	66.5	-	-	79.4	43.4	-
Run 4	-	-	-	-	93.1	44.8	-
AVERAGE	57.6	64.2	62.1	66.3	83.1	45.0	125.4
Ultimate Tensile Strength (MPa)							
Run 1	118.0	96.4	100.0	95.5	169.9	111.0	187.5
Run 2	-	95.5	117.2	99.9	176.7	113.2	162.4
Run 3	-	89.7	-	-	166.5	113.4	-
Run 4	-	-	-	-	162.1	117.2	-
AVERAGE	118.0	93.9	108.6	97.70	168.8	113.6	175.0
Elongation %							
Run 1	5.7	4.6	3.1	1.9	5.6	10.5	1.3
Run 2	-	-	5.5	2.6	11.0	11.3	0.9
Run 3	-	2.5	-	-	8.7	11.0	-

EXAMPLE	13	14	15	16	C14	C15	C16
Run 4	-	-	-	-	9.0	3.0	-
AVERAGE	5.7%	3.6%	4.3%	2.3%	8.6%	9.0%	1.1%

By way of the average tensile properties values shown in Table 5, it can be seen that the permanent mold cast alloys of the present invention (i.e., Examples 13 to 16) demonstrate improved yield strength at 150°C when compared to magnesium alloy AE42 (i.e., C15).

Having thus described the invention, what is claimed is:

CLAIMS

1. A magnesium-based casting alloy having improved elevated temperature performance which comprises, in weight percent, 2 to 9% aluminum and 0.5 to 7% strontium with the balance being magnesium except for impurities commonly found in magnesium alloys.
2. The magnesium-based casting alloy of Claim 1, wherein said alloy comprises 4 to 6% aluminum.
3. The magnesium-based casting alloy of Claim 1, wherein said alloy comprises 4.5 to 5.5% aluminum.
4. The magnesium-based casting alloy of Claim 1, wherein said alloy comprises 1 to 5% strontium.
5. The magnesium-based casting alloy of Claim 1, wherein said alloy comprises 1 to 3% strontium.
6. The magnesium-based casting alloy of Claim 1, wherein said alloy comprises 1.2 to 2.2% strontium.
7. The magnesium-based casting alloy of Claim 1, wherein said alloy has a structure including a matrix of grains of magnesium having a mean particle size of from about 10 to about 200 μm reinforced by intermetallic compounds having a mean particle size of from about 2 to about 100 μm .
8. The magnesium-based casting alloy of Claim 1, wherein said alloy is a diecast alloy having an average % creep deformation at 150°C of less than or equal to 0.06%, an average bolt-load-loss at 150°C of less than or equal to 6.3°, and an average tensile yield strength at 150°C of greater than 100MPa.

9. The magnesium-based casting alloy of Claim 1, wherein said alloy is a permanent-mold cast alloy having an average % creep deformation at 150°C of less than or equal to 0.03%, an average bolt-load-loss at 150°C of less than or equal to 3.75°, and an average tensile yield strength at 150°C of greater than 57MPa.

10. A magnesium-based casting alloy having improved elevated temperature performance which comprises, in weight percent, 2-to 9% aluminum, 0.5 to 7% strontium, 0 to 0.60% manganese, and 0 to 0.35% zinc, with the balance being magnesium except for impurities commonly found in magnesium alloys.

11. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 4 to 6% aluminum.

12. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 4.5 to 5.5% aluminum.

13. The magnesium-based casting alloy of Claim 10, where said alloy comprises 1 to 5% strontium.

14. The magnesium-based casting alloy of Claim 10, where said alloy comprises 1 to 3% strontium.

15. The magnesium-based casting alloy of Claim 10, where 20 said alloy comprises 1.2 to 2.2% strontium.

16. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 0.25 to 0.35% manganese.

17. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 0.28 to 0.35% manganese.

25 18. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 0 to 0.1% zinc.

19. The magnesium-based casting alloy of Claim 10, wherein said alloy comprises 0 to 0.05% zinc.

20. The magnesium-based casting alloy of Claim 10, wherein said alloy has a structure including a matrix of grains of magnesium having a mean particle size of from about 10 to about 200 μm reinforced by intermetallic compounds having a mean particle size of from about 2 to about 5 100 μm .

21. The magnesium-based casting alloy of Claim 10, wherein said alloy is a diecast alloy having an average % creep deformation at 150°C of less than or equal to 0.06%, an average bolt-load-loss at 150°C of less than or equal to 6.3°, and an average tensile yield strength at 150°C 10 of greater than 100MPa.

22. The magnesium-based casting alloy of Claim 10, wherein said alloy is a permanent-mold cast alloy having an average % creep deformation at 150°C of less than or equal to 0.03%, an average bolt-load-loss at 150°C of less than or equal to 3.75°, and an average tensile yield 15 strength at 150°C of greater than 57MPa.

23. A magnesium-based casting alloy comprising, in weight percent, 4 to 6% aluminum, 1 to 5% strontium, 0.25 to 0.35% manganese, and 0 to 0.1% zinc with the balance being magnesium except for impurities commonly found in magnesium alloys.

20 24. The magnesium-based casting alloy of Claim 23, wherein said alloy has a structure including a matrix of grains of magnesium having a mean particle size of from about 10 to about 200 μm reinforced by intermetallic compounds having a mean particle size of from about 2 to about 100 μm .

25 25. The magnesium-based casting alloy of Claim 23, wherein said alloy is a diecast alloy having an average % creep deformation at 150°C of less than or equal to 0.06%, an average bolt-load-loss at 150°C

of less than or equal to 6.3°, and an average tensile yield strength at 150°C of greater than 100MPa.

26. The magnesium-based casting alloy of Claim 23, wherein said alloy is a permanent-mold cast alloy having an average % creep deformation at 150°C of less than or equal to 0.03%, an average bolt-load-loss at 150°C of less than or equal to 3.75°, and an average tensile yield strength at 150°C of greater than 57MPa.

27. A magnesium-based casting alloy comprising, in weight percent, 4 to 6% aluminum, 1 to 3% strontium, 0.25 to 0.35% manganese, and 0 to 0.1% zinc with the balance being magnesium except for impurities commonly found in magnesium alloys.

28. A magnesium-based casting alloy comprising, in weight percent, 4.5 to 5.5% aluminum, 1.2 to 2.2% strontium, 0.28 to 0.35% manganese, and 0 to 0.05% zinc with the balance being magnesium except for impurities commonly found in magnesium alloys.

INTERNATIONAL SEARCH REPORT

National Application No.

PCT/CA 00/01527

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22C23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 340 416 A (SHIBATA TOSHIKUKE ET AL) 23 August 1994 (1994-08-23) table 2 ---	1-28
X	EP 0 665 299 A (MAZDA MOTOR) 2 August 1995 (1995-08-02) page 3, line 52 -page 4, line 7 page 5, line 37 - line 40 --- -/-	1-28

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

6 April 2001

Date of mailing of the international search report

25/04/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax (+31-70) 340-3016

Authorized officer

Ashley, G

INTERNATIONAL SEARCH REPORT

national Application No
PCT/CA 00/01527

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHEMICAL ABSTRACTS, vol. 119, no. 18, 1 November 1993 (1993-11-01) Columbus, Ohio, US; abstract no. 186048, NUSSBAUM, G. ET AL: "New magnesium-aluminum based alloys with improved casting and corrosion properties" XP002164886 abstract & MAGNESIUM ALLOYS THEIR APPL., 'PAP. DGM CONF.! (1992), 351-8. EDITOR(S): MORDIKE, BARRY L.; HEHMAN, FRANZ. PUBLISHER: DGM INFORMATIONSGES., OBERURSEL, GERMANY. ,</p>	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No:

PCT/CA 00/01527

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5340416 A	23-08-1994	JP	3110117 B	20-11-2000
		JP	5171331 A	09-07-1993
		DE	69221712 D	25-09-1997
		DE	69221712 T	12-02-1998
		EP	0549998 A	07-07-1993
EP 0665299 A	02-08-1995	JP	7224344 A	22-08-1995
		DE	69423335 D	13-04-2000
		DE	69423335 T	30-11-2000
		US	6143097 A	07-11-2000

1 / 4

BEST AVAILABLE COPY

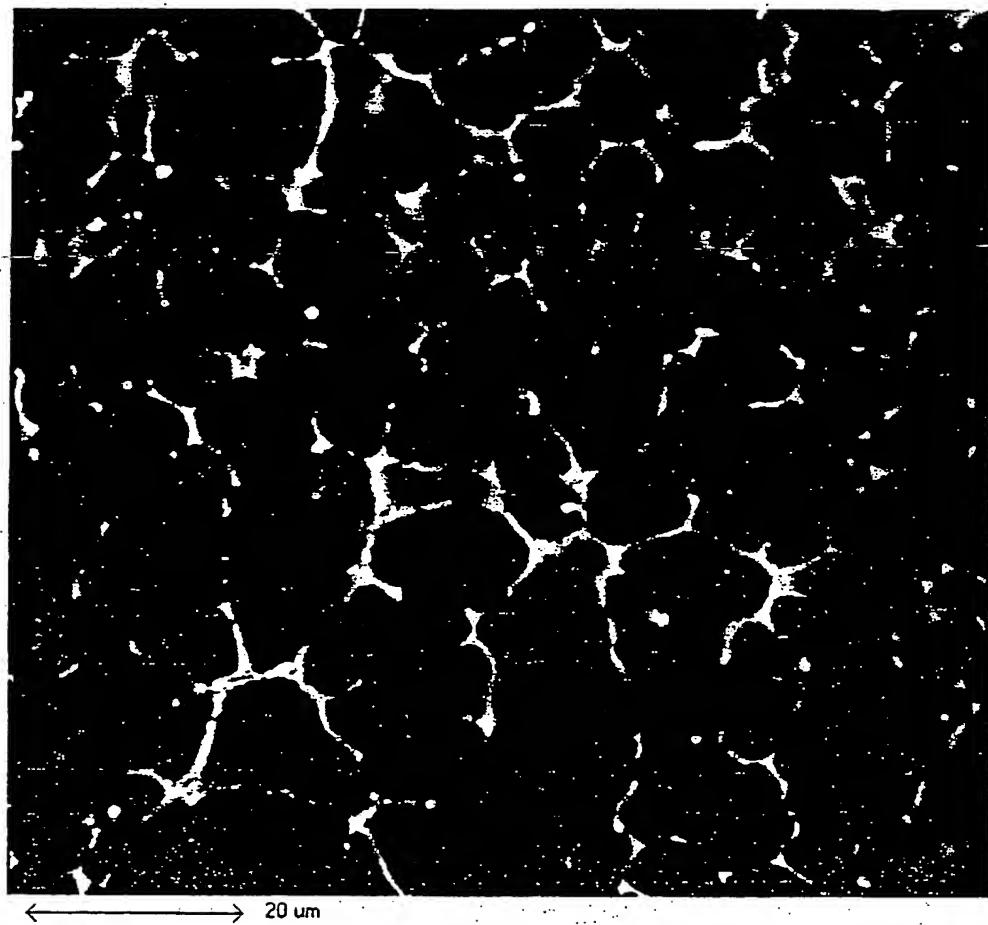


FIG. 1

2 / 4

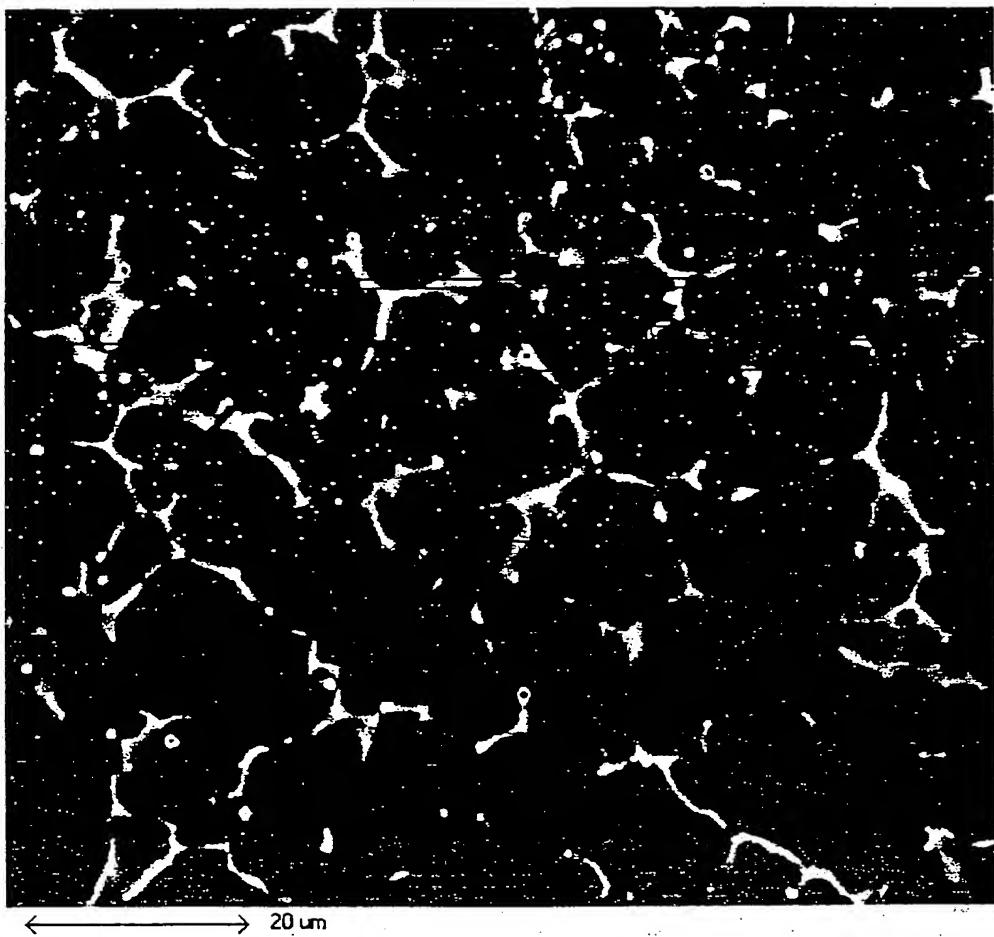


FIG. 2

3 / 4

BEST AVAILABLE COPY

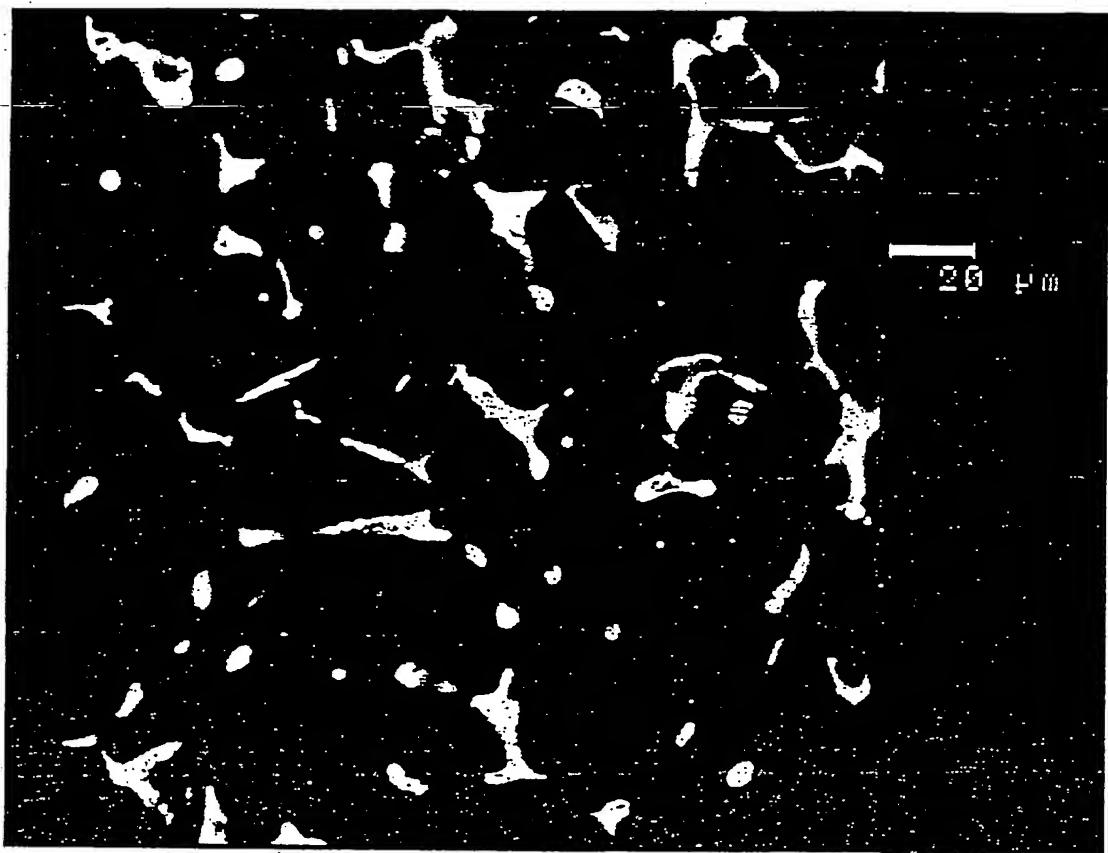


FIG. 3

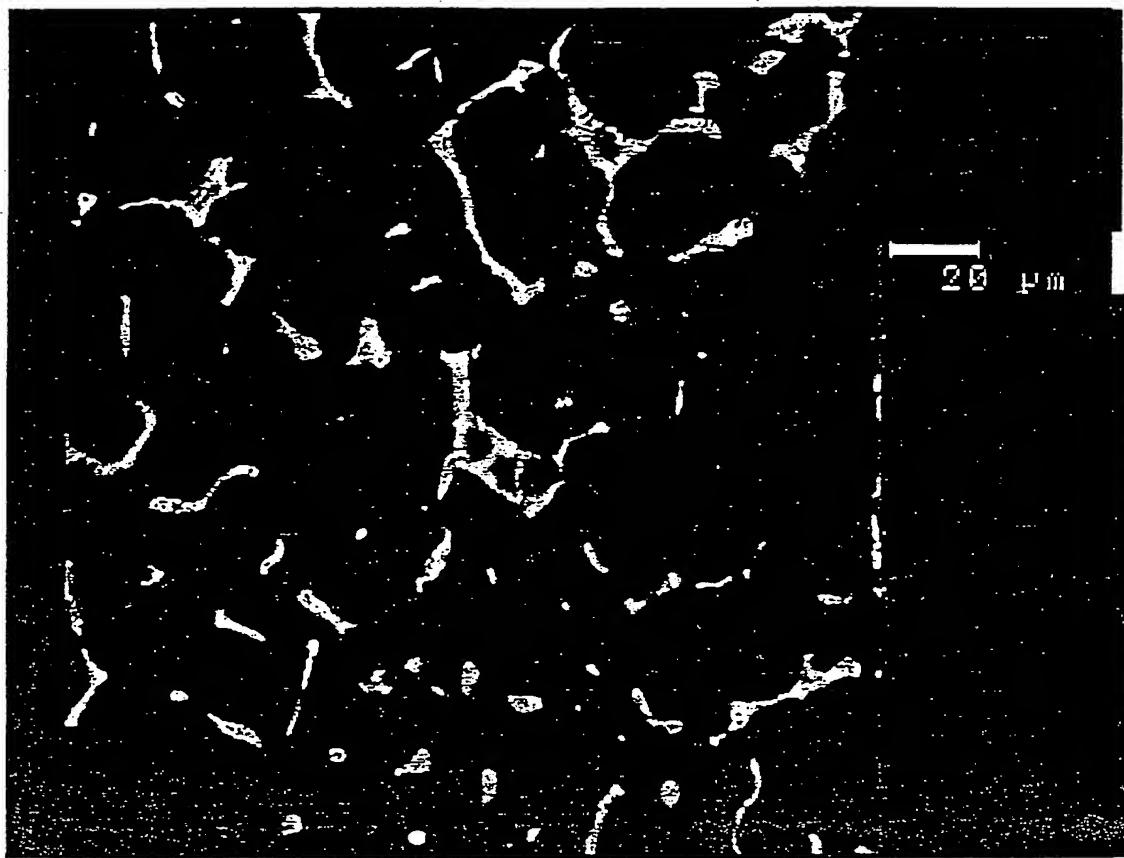


FIG. 4